

# **Effect of High Doses of Chemical Admixtures on the Freeze–Thaw Durability of Portland Cement Concrete**

Charles Korhonen

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**Abstract:** The usual approach to increasing concrete's resistance to freeze-thaw damage is to modify its microstructure. Because concrete readily absorbs water, when it is in a wet environment and then cooled to below 0°C, any water that freezes inside the concrete will expand and, depending on the nature of the internal pore structure, could lead to internal micro-cracks. A single freezing event does not cause much harm, but repeated freezing and thawing cause the tiny cracks to grow and ultimately result in conspicuous cracks on the surface of the concrete, known as frost damage. This weakens the concrete and reduces its service life. There are several mechanisms responsi-

ble for this damage, so preventing it is complex. However, there are several practical methods used today to counteract problems caused by freezing water, including 1) incorporating entrained air into the concrete to relieve pressures caused by freezing water, 2) using low water-to-cement ratios to minimize the type of voids in which water typically freezes, and 3) using silica fume to refine the pore system so that water may not be able to freeze at normal ambient temperatures. This report reviews the frost damage mechanisms, considers the usefulness of current prevention techniques, and advances a new approach for making concrete resist the deleterious effects of freezing and thawing.

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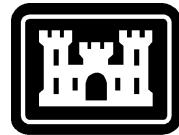
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Charles Korhonen

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Prepared for  
OFFICE OF THE CHIEF OF ENGINEERS

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## PREFACE

This report was prepared by Charles J. Korhonen, Research Civil Engineer, Civil and Infrastructure Engineering Branch, Engineer Research and Development Center (ERDC), U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Hanover, NH. The author thanks Tim McDowell, Wyoming Department of Transportation, and Ray Rollings, CRREL, for their reviews. Funding for this work was provided by DA Project 4A762784AT42, *Military Engineering Technology; Airfields and Pavements in Cold Regions—Force Projection*; Work Package 227; Work Unit AT42-AP-001.

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# **Effect of High Doses of Chemical Admixtures on the Freeze–Thaw Durability of Portland Cement Concrete**

CHARLES KORHONEN

## **1 INTRODUCTION**

Concrete is the backbone of modern construction. The United States produces more than 800 million tons of concrete every year, and of that, approximately 300 million tons goes into our nation's highways (Suprenant and Malisch 1999). That's nearly one and a half cubic yards of concrete for each U.S citizen every year, or said another way, it's close to 1% of our gross domestic product. Concrete seemingly is used everywhere, largely because it is inexpensive, readily available, and strong. By weight, concrete makes up more than half our nation's infrastructure consisting of bridges, pavements, and buildings. However, despite its popularity, concrete is not indestructible. Sixty percent of our nation's roads need repair, and more than 40% of our bridges are structurally deficient or functionally obsolete (Civil Engineering Research Foundation 1994). In northern climates, concrete's most persistent problem, whether it is in horizontal or vertical construction, is deterioration caused by freezing and thawing (Cordon 1966). Since concrete readily absorbs water, it is vulnerable to damage if the water within its system of pores can freeze and generate disruptive pressures. There are various ways to improve the resistance of concrete. Usually concrete made with good aggregate, a low water-to-cement ratio, and air entrainment will have good resistance to cycles of freezing and thawing. But even with these features in place, deterioration to the infrastructure continues to occur and is mounting faster than it can be repaired. The U.S. spends about \$80 billion per year on infrastructure construction and rehabilitation projects (Civil Engineering Research Foundation 1993), but the estimate to repair existing deficiencies is over a trillion dollars (Sedgwick 1991).

The condition of the infrastructure will worsen unless current efforts are intensified or unless a more durable concrete can be produced so that, when it is put in place, it will last longer. Though spending more maintenance dollars is one solution—an expensive one—the durability of concrete would not have to be

significantly improved to have a major effect on repair bills. The Transportation Research Board recently estimated that if the durability of our roads and bridges were improved by as little as 1%, the U.S. could save up to \$30 billion in repair bills in 20 years (Civil Engineering Research Foundation 1993). Durability issues include corrosion to metals, chemical reactions in pavements, and damage caused by thermal cycling. For northern climates, an incremental improvement in the freeze-thaw durability of concrete should provide a significant savings in repair bills. Consequently the challenge to northern engineers is to devise a better way to control the mechanisms that lead to frost damage in concrete.

This report reviews what is known about freeze-thaw mechanisms. Concrete contains a complex structure of pores that form during the curing process. Depending on how they form, the pores affect the amount of water that can freeze and thus the potential destructive internal stresses that can develop. The report considers the development of the pore structure in portland cement concrete as it cures, addresses the features that influence frost damage, and takes into account the mechanisms that are thought to cause the problem. Finally the report searches recent advances in concrete durability and recommends needed research to make concrete last longer in a freeze-thaw environment.

## 2 PORE STRUCTURE

Concrete, in its simplest form, is composed of cement, aggregate (gravel and sand), and water. A chemical reaction between the cement and the water forms a paste that, when hardened, binds the aggregate together to give concrete its characteristic strength. For practical purposes, concrete can be thought of as a two-phased composite consisting of cement paste and aggregate, each which can be treated separately when considering frost action (ACI 2001). Simplifying this picture further, whenever aggregates used to make concrete meet ASTM C 33 requirements, the question of whether the concrete is resistant to freezing and thawing rests only with the quality of the hardened paste. Hence, the development of pore structure inside cement paste is fundamental to understanding the freeze–thaw resistance of concrete and therefore is a focus of this report.

When portland cement is dispersed in water, the cement immediately begins to ionize and precipitate into various new products through a chemical process called hydration. The most critical products thus formed are calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). C-S-H is an amorphous compound whose stoichiometry depends on the temperature, time, and moisture conditions during curing. It occupies about two-thirds the volume of all hydration products and consists of extremely small, tightly spaced sheets or layers that resemble crumpled paper (Brunauer 1962). Because of its smallness, C-S-H has enormous surface area, on the order of 100–700 m<sup>2</sup>/g (Feldman and Sereda 1970), wherein lies the secret of concrete's strength. When viewed under an electron microscope, C-S-H looks like sea anemones with tentacles reaching out in all directions. Because of the very large surface areas, the strength of concrete is derived from van der Waals forces attracting tentacles from one hydration site to tentacles at another. Though other bonds exist in cement paste, surface effects predominate, so that concrete is largely held together by what amounts to electrostatic cling. This probably explains why concrete is strong in compression but weak in tension. In contrast, CH forms large, well-defined hexagonal crystals, which account for 20–25% of the hydrated paste. Because of their size, significantly less surface area is involved and thus van der Waals forces are less available for binding action, so they contribute little to the strength of concrete. Calcium sulfoaluminate, a third product, which eventually converts into monosulfoaluminate once all the gypsum originally added to the anhydrous cement is used up, makes up 15–20% of the paste. These sulfate compounds, together with the minor amount of ferrite phases that also develop, are not believed to affect the frost resistance of hardened cement paste and are not considered in this report.

Cement paste, when fully hydrated, is not solid but contains numerous pores of various sizes throughout its matrix. Powers conducted the research that forms

our basic understanding about the development of pore structure in cement paste (Powers and Brownyard 1946-47, Powers 1949, Powers and Helmuth 1953). During hydration, cement chemically combines with up to 23% water by weight (Hewlett 1998), depending on the completeness of hydration, and it becomes 2.1 times larger than its original absolute volume (Neville 1988). The hydrated cement is often referred to as cement gel, which has a characteristic porosity of about 28% (Mindess and Young 1981). Since hydrating cement will only grow into unoccupied space—it does not exert outward pressure—it can be calculated that cement must combine with at least 36% water by weight to provide the necessary space into which the cement can swell (Powers and Brownyard 1946-47). However, if there is no outside water available to replenish that used up by hydration, a cement paste with a 0.36 water-to-cement ratio will cease hydrating when about 85% of the cement has hydrated because of self-desiccation. This does not adversely affect strength, as unhydrated cement can perform quite nicely as aggregate, but to provide the space and the water for complete hydration, the water-to-cement ratio must be at least 0.42.

Cement's pore structure develops by the gradual growth of gel into the space originally occupied by the anhydrous cement and mixing water. As long as the initial water-to-cement ratio is at or below 0.36, the porosity of the cement paste will decline with progressing hydration until all available water is used up and the porosity remaining is that of the gel. At water-to-cement ratios above 0.36, the gel will not fill all available space, so the porosity of the paste becomes part of the gel plus part of the water-filled space not filled by gel. The part of the paste left unfilled by hydration products is called capillary porosity, and the higher the initial water-to-cement ratio, the greater the capillary pore volume. Accordingly the porosity of hydrated cement paste consists of two types of pores: gel and capillary.

Size and distribution are the two critical factors that characterize the porosity of hydrated cement paste when freeze-thaw durability is of concern. The porosity of hydrated cement gel is fixed. As long as some cement hydrates, the resulting product will contain a characteristic porosity of 28%. The interlayer spaces within the gel (C-S-H structure) are the smallest pores in hydrated paste. Because of surface tension effects, gel pores will imbibe water from larger pores and, under natural conditions, are nearly always filled with water. However, as will be discussed later, gel pores are so tiny that water in them will not freeze at ordinary ambient temperatures. Capillary pores, on the other hand, are much larger, and the water in them freezes quite easily. Capillary porosity is entirely dependent on the water-to-cement ratio because it defines the space that must be filled by the hydration products. Though all pores in cement paste are interconnected, capillary pores are mainly responsible for any appreciable movement of water through the paste and, as we will see, for its vulnerability to frost damage.

### 3 FREEZE–THAW MECHANISMS

Several theories have been advanced over the years to explain how thermal cycling below the freezing point of water leads to frost damage in concrete (Podvalnyi 1976). Before we explore them, it is important to know that dry concrete is unaffected by repeated cycles of freezing and thawing. Thus, provided the aggregates are durable, the susceptibility of concrete to frost action depends on whether the hardened paste contains water—and how much of it—and if that water can freeze to generate sufficient stresses to damage the interior of the concrete.

Perhaps the first explanation of frost damage came from the observation that glass bottles full of milk broke apart when left outdoors during cold weather. Since the density of ice is 0.9167 g/cm<sup>3</sup> (Ginnings and Corruccini 1947), it follows that a closed container, such as a milk bottle, would break apart if it initially contained more than 91.7% water by volume. The pressures that might develop inside the milk bottle can be estimated from the Clapeyron equation as developed by Pitzer (Pitzer and Brewer 1961) for the equilibrium condition between ice and water and as explained by Barrow (1988):

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad (1)$$

where  $P$  = pressure  
 $T$  = melting temperature  
 $H$  = heat of fusion  
 $V$  = volume.

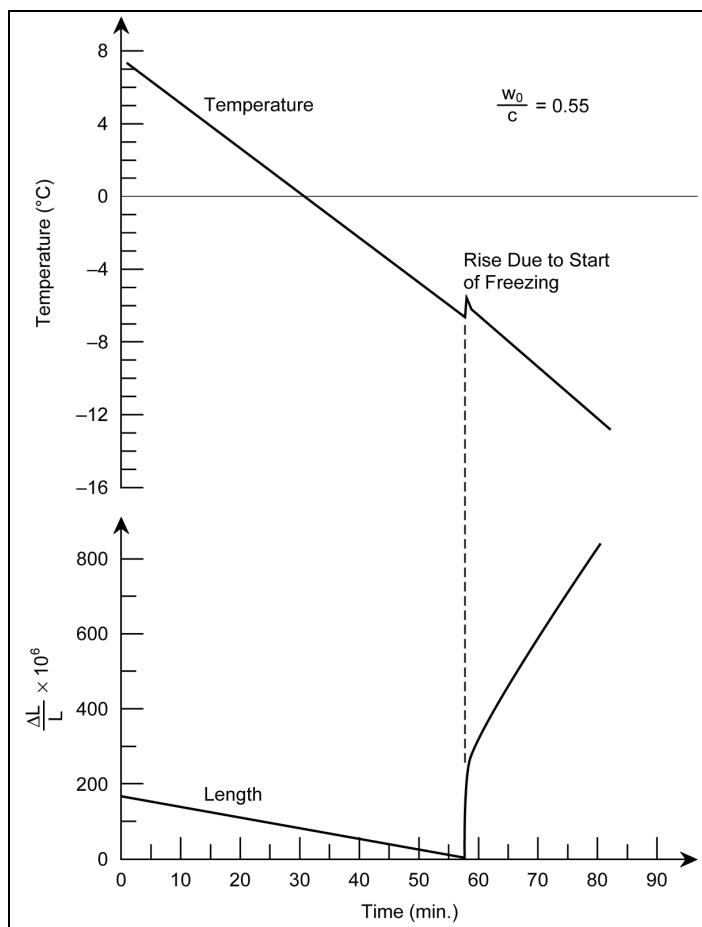
Assuming the melting temperature of pure ice to remain constant (273 K) (a good approximation for this exercise) and inserting values into eq 1 for ordinary heat of fusion (333,000 J/kg), melting temperature at STP, and volume increase (0.0905 cm<sup>3</sup>) for water at its liquid–solid phase change shows that the milk bottle, if filled with water, would have to resist approximately 13 MPa to prevent freezing. Thus, even at –1°C, the pressure caused by freezing water can easily break brittle construction materials, such as pore walls inside concrete with tensile strengths around 7 MPa.

Collins (1944) proposed another explanation for frost damage by observing the condition of concrete pavements in England. He noted that the pavements were not of the best quality when cast, but because they had been exposed to a very cold winter with extended periods of below-freezing temperatures, he concluded that Taber's (1929, 1930a,b) description of ice lenses in soils was the

mechanism of damage in this case. Collins felt that since the concrete had a coarse porosity, it was somewhat analogous to soil, which also has a coarse porosity. The main difference was that soils consist of loosely packed particles that contact at discrete locations, whereas concrete is a solid with holes in it. Taber demonstrated that soil, when unidirectionally cooled, would grow ice lenses perpendicular to the direction of heat flow. He found that this growth of ice exerted considerable pressure that was dependent on a nearby supply of unfrozen water. Taber characterized ice lens growth in soils as being caused by the osmotic potential between water and ice. Collins observed ice lenses in concrete pavements, adding credibility to this theory.

Powers (1945), an initial supporter of the “milk bottle” theory, proposed an alternate explanation. He reasoned that concrete usually contains enough air voids to accommodate all the ice that can possibly form inside fully saturated concrete. Yet concrete suffers frost damage, which suggested to him that the mere 9% expansion of water turning into ice was not the lone cause of this damage. He proposed, consequently, that as ice grows in water-filled pores, the sudden volume increase compresses unfrozen water against the pore walls, forcing it out of the pores through smaller pores. This forced flow of water appeared to be a reasonable explanation of frost damage. Since the pressure of water flowing through a pipe, for example, directly depends on the flow rate and path length, Powers figured that pore water could not flow any farther than 0.25 mm under normal cooling rates without overstressing the walls of the pores through which the water was escaping. Further refinement of this work has provided the now-familiar air bubble spacing factor of 0.2 mm.

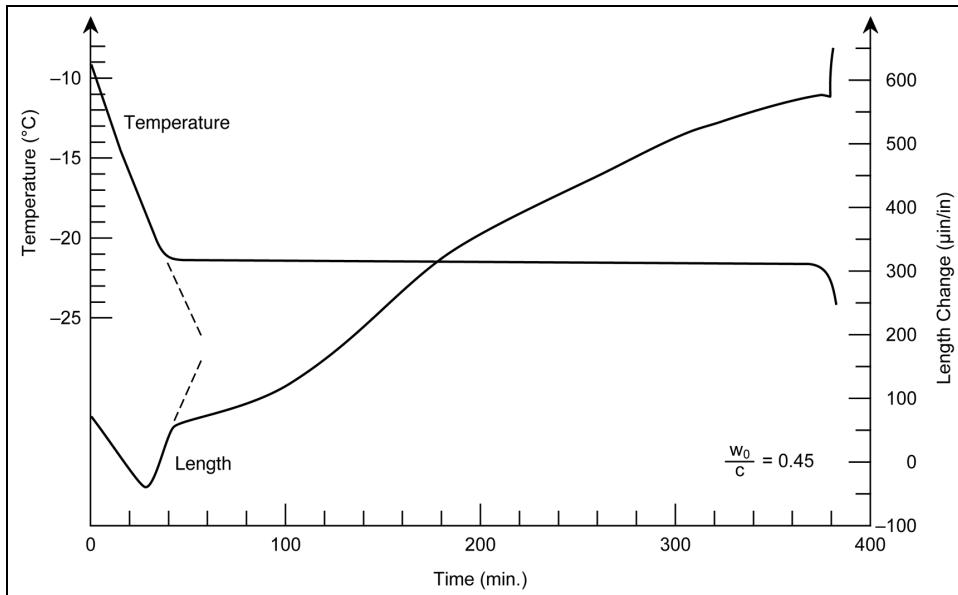
Through extensive experiments, Powers and Helmuth (1953) strengthened the case for hydraulic pressure but, at the same time, realized that there were other mechanisms for frost damage as well. Their observation that a specimen of non-air-entrained paste shrinks until the moment freezing occurs, when it suddenly expands, provides a compelling argument for hydraulic pressure. Since freezing happens quickly, it follows that unfrozen water would have to flow away from the freezing site quickly, all of which would lead to high hydraulic pressure. No other theory has been able to explain the sudden expansion shown in Figure 1. Their realization that hydraulic pressure was not the lone cause of frost damage came when they observed these same pastes to continue to expand as the temperature was held constant. The cause of the continued growth shown in Figure 2 was attributed to unfrozen water flowing toward the freezing sites, rather than away from them. (Not all water in paste freezes at the same temperature, which creates the potential for unfrozen water in concrete at low temperatures.) As the specimen is cooled, water that remains unfrozen is of higher free energy than the ice already formed, so the water flows toward the ice. This



**Figure 1. Sudden expansion at the moment of freezing of non-air-entrained paste, strongly suggesting that hydraulic pressure created by water being forced away from freezing sites is the cause of frost damage to cement paste. (After Powers and Helmuth 1953.)**

process is much like osmosis and potentially can lead to expansive pressures. This mechanism uses the basic principles of ice growth in soils. Expansion occurs even when non-expanding fluids such as benzene are used in place of water, demonstrating that hydraulic pressure is not the lone cause of frost damage (Beaudoin and MacInnis 1974).

Concerning osmosis, it is well known that pore water contains dissolved alkalis, creating a solution that freezes at a lower temperature than does pure water. Since the solid that freezes from such a solution is pure ice, the concentration of alkalis increases in the water next to newly formed ice. This immediately sets up a process in which water molecules in more dilute solutions farther away



**Figure 2. Continued expansion of non-air-entrained paste at constant temperature, suggesting that water is flowing toward the freezing site(s) rather than away. (After Powers and Helmuth 1953.)**

from the ice migrate toward the ice in an attempt to reach equilibrium. Osmotic pressures of even quite dilute solutions are on the order of several megaPascals (Eastman 1970) and result in one more component of expansive pressure. Powers and Helmuth pointed out that freezing-induced osmotic pressure increases with the concentration of the pore water solution.

There are several other theories for frost damage. Litvan (1980) provided the most interesting of these, speculating that ice formation may not be necessary for damage to occur, just low temperatures. He suggested that water will migrate, under vapor pressure, to locations where it can freeze, whether it is to larger pores or to the exterior. The problem arises when the concrete thaws and the desorbed water tries to return to its original position but sometimes can't. This seems to be a variation of the hydraulic pressure theory and the ice lens theory combined.

As can be seen, frost damage to concrete is not completely understood. It could be caused by hydraulic or osmotic pressure, desorption-absorption discontinuities, ice lens growth, or some combination of these or other theories. The commonalities, however, to all of the theories are the pore structure of the cement paste and the presence of freezable water. Modifying one of these commonalities affects the resulting concrete's durability, perhaps making it completely immune to frost damage. Thus, these two factors provide the keys for dealing with the frost resistance of concrete.

## 4 EFFECT OF MODIFYING THE PORE STRUCTURE

Given that concrete readily absorbs water, it is unremarkable that concrete should be damaged by cycles of freezing and thawing. As we have seen, there are several theories that explain why this is so, but for practical purposes the common approach to avoiding or at least minimizing the problem is to modify the pore structure of the cement paste. This is done for two reasons: 1) to minimize the amount of freezable water that can occupy the paste and 2) to assure that any water that does freeze does not overstress the system. Several factors are crucial to achieving a frost-resistant concrete using this approach.

### Water-to-Cement Ratio

The primary influence of water-to-cement (w/c) ratio on the freeze–thaw durability of concrete is its effect on capillary pore volume, i.e., its permeability and ability to absorb freezable water. As previously discussed, when it's above a certain value, each increase in w/c produces more capillary voids, both in volume and in size. And as we'll see, it's pore size that determines if water can freeze within concrete.

When a saturated material possessing a continuous range of pore sizes is subjected to low temperatures, according to thermodynamics, the amount of water that freezes depends on the temperature and on the size of the pores. Skapski et al.(1957) presented a useful equation that relates pore size to the temperature at which water freezes:

$$T = \frac{-2T_m \gamma_{iw}}{H_f r \rho_i} \quad (2)$$

where  $T_m = 273$  K

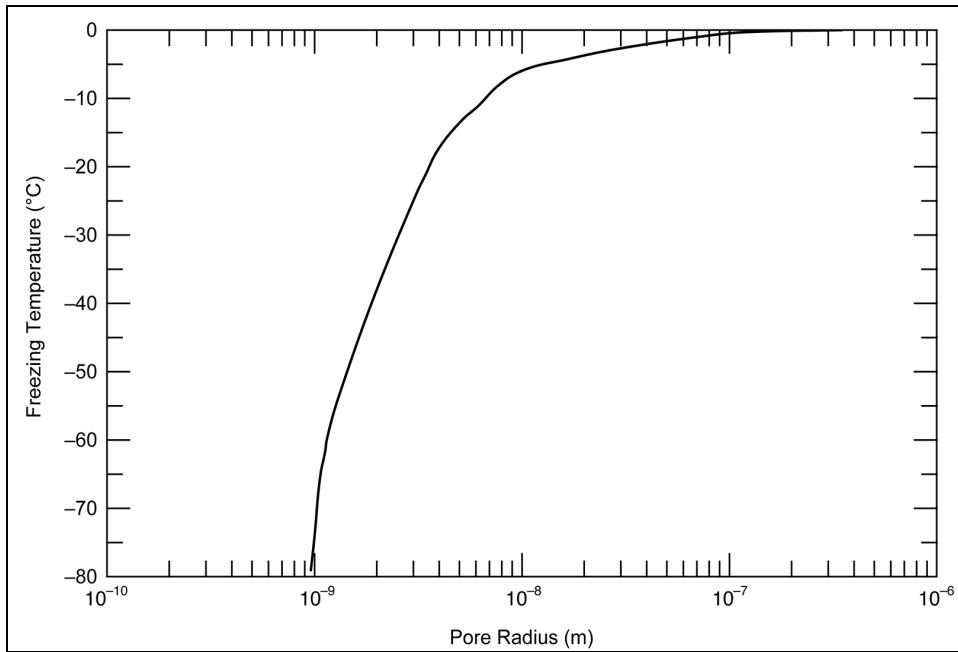
$\gamma_{iw}$  = surface tension between water and ice (0.031 N/m)

$H_f$  = normal heat of fusion (333,000 J/kg)

$r$  = ice crystal radius (mm)

$\rho_i$  = density of ice (917 kg/m<sup>3</sup>).

However, to use this equation it must be realized that there remains a layer of unfrozen water adsorbed on the walls of the pore. The thickness of the layer, which varies slightly with temperature, amounts to about four molecular layers of water, where a water molecule measures about  $3.1 \times 10^{-10}$  m in diameter (Helmuth 1960). Hence, to the results of eq 2 must be added about  $12 \times 10^{-10}$  to obtain the true radius of the pore. Figure 3 is a plot of ice crystal size, adjusted for the liquid layer. Since winter temperatures rarely drop below  $-40^{\circ}\text{C}$ , it is



**Figure 3. Freezing temperature vs. pore radius.**

clear from Figure 3 that water in pores smaller than 0.0033  $\mu\text{m}$  cannot freeze. Mehta (1986) showed that pore sizes in cement paste run from 0.02–10  $\mu\text{m}$  for capillary pores to 0.0005–0.01  $\mu\text{m}$  for gel pores. Clearly only capillary voids and some larger gel pores can freeze. Thus, capillary-size pores are critical to the frost resistance of concrete.

Capillary voids also greatly affect permeability. According to Powers (1958a) the effect of gel porosity on permeability is negligible compared to capillary porosity. At w/c values above 0.50, the coefficient of permeability is highly dependent on water content; relatively small increases in water content result in large increases in permeability. The ease with which water can move within cement paste influences the hydraulic pressure that can result because of freezing and is a factor of great importance in connection with freeze-thaw durability, especially when combined with the rate of cooling.

### Cooling Rate

It is generally accepted that the faster the cooling rate, the more damage will occur. This is especially true when hydraulic pressures are considered to be important, as the pressure that is produced within a specimen depends on the rate of water movement within the paste. Litvan (1976) demonstrated that 0.70-w/c samples dilated considerably more when cooled at 20°C/hr than did similar

samples cooled at 2.5°C/hr. Similarly Pigeon et al. (1985) noted that changing the cooling rate from 2° to 6°C/hr has a significant detrimental influence on freeze–thaw durability. However, in some situations, cooling rate may not be so important. For example, Fontenay and Sellevold (1980) found in calorimetric studies of paste that the total amount of ice formed is independent of the cooling rate but also that the amount of ice formed per unit time is affected by the cooling rate. Fagerlund (1992) has advanced the idea that cooling rate may not be a factor when the material is sealed—a factor that Korhonen and Charest (1995) used when designing a cryogenic test for the frost resistance of aggregates. Until freeze–thaw action is better understood, it is best to use data gathered from like cooling rates when comparing one concrete against another.

### Degree of Saturation

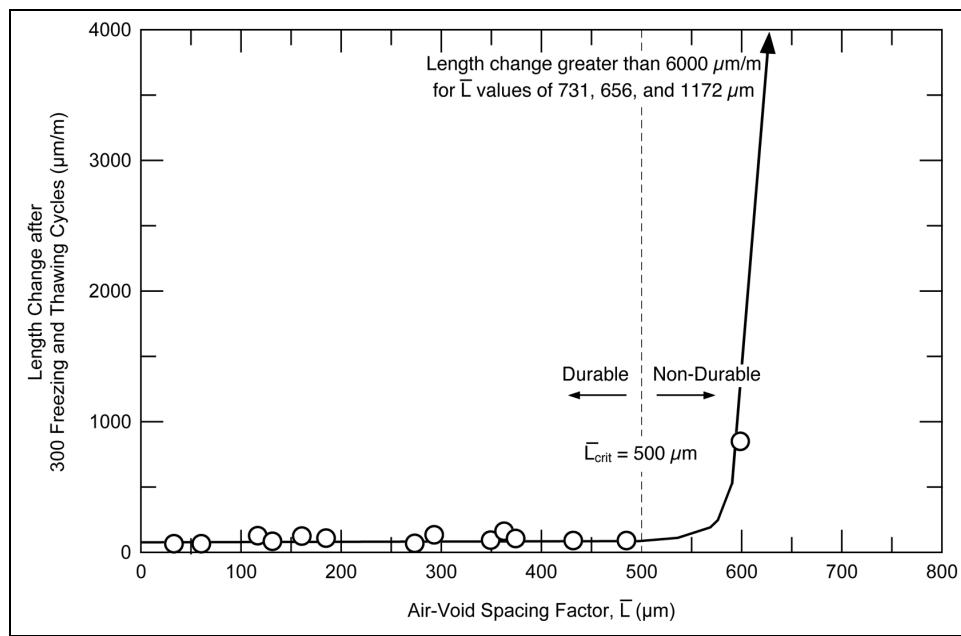
Though seemingly trivial, it is important to know that partially dry concrete is extremely resistant to cycles of freezing and thawing. Some experts feel that below certain water contents, concrete is immune to frost damage. Whiteside and Sweet (1950) showed that samples more than 91% saturated were easily damaged by freeze–thaw cycles but were difficult to damage when they contained less than 87% water, calculated as the percent of water absorbed during submersion in water. From experiments conducted on non-air-entrained concrete, Fagerlund (1977) reported that the critical degree of saturation is about 80%. He pointed out that, in practice, concrete may never attain this much water, so critical saturation alone is not a measure of frost resistance. It is interesting to note that the concrete in Fagerlund’s study was not immune to damage at water contents below 80%, which suggests that partially dry concrete, though very resistant to frost damage, will eventually disintegrate.

### Air Bubbles

Until now, we have focused on cement paste with its two types of voids. Air bubbles, a third class of voids, are physically incorporated into the paste during mechanical mixing and are not considered an inherent part of cement paste. There are two kinds of air bubbles in the paste matrix of concrete: entrapped and entrained. Entrapped air bubbles are unintentionally included in the paste during the mixing process, and entrained air bubbles are purposely incorporated into the paste with the help of chemical admixtures. It was by accident that the value of entrained air was discovered. In the late 1930s beef tallow, which was being used as a grinding aid in cement production, was found to make concrete much more resistant to frost action. The tallow stabilized the air normally entrapped in the concrete so that more of it remained in the final product rather than disappearing.

Cook (1952) observed that in order for concrete to withstand more than one winter it must contain entrained air. Powers (1958b) demonstrated the benefit of air for the frost resistance of concrete. In a series of experiments, he pointed out that de-aired paste elongated by 1600 microstrain during freezing to  $-24^{\circ}\text{C}$  and retained a residual strain of 500 microstrain after thawing. When 2% air was entrained into the paste, it elongated 900 microstrain with a residual strain of 300 microstrain, but paste with 10% air showed no elongation on freezing and no residual strain on thawing. It has since been established that when air is intentionally incorporated to around 4–8% of the volume of fresh concrete, the resulting hardened concrete will have good durability.

Another requirement is that the air bubbles must be properly spaced so as to allow unfrozen water, expelled from a capillary during freezing, to reach an air void without overstressing the matrix. The so-called spacing factor is considered to be the most important gauge of concrete durability. Figure 4 illustrates this concept for concrete that has a w/c of 0.5 and was cured and tested according to ASTM C 666, procedure A (ASTM 1984). Durability remained good until the average distance between bubbles exceeded 500  $\mu\text{m}$ , when it became poor. The

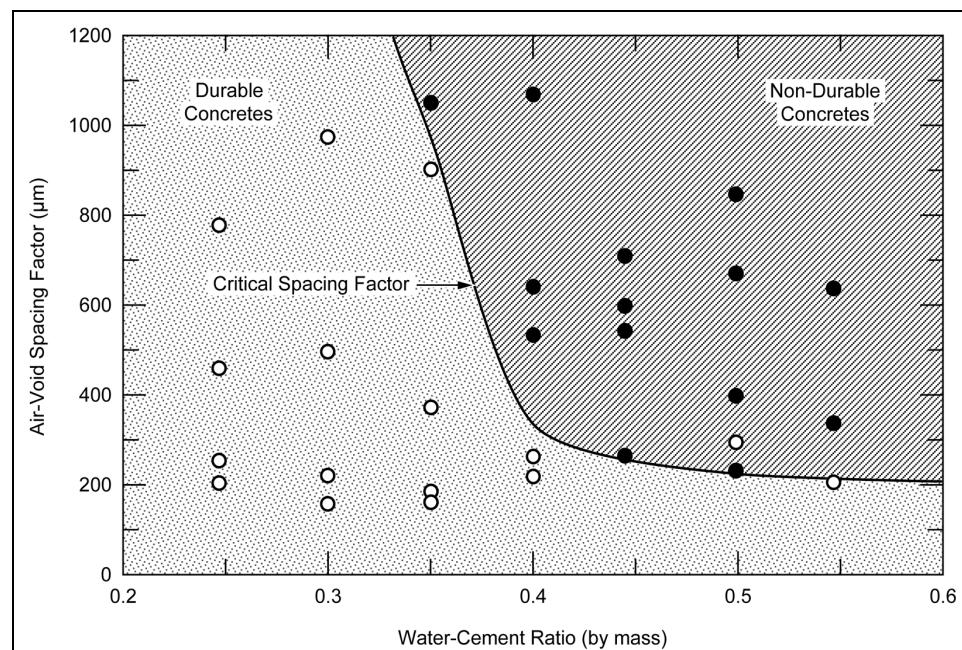


**Figure 4. Length change after 300 freezing and thawing cycles as a function of the average distance between air bubbles. (After Pigeon et al. 1986.)**

critical spacing factor of 200  $\mu\text{m}$  recommended by ACI (1990) is what most specifications target for concrete placed in the U.S. today. Although somewhat larger values may be allowed for mild climates, smaller values can weaken the concrete because of the increased air content necessary. To some extent, entrained air bubbles counteract the effect of lower water contents, but a rule of thumb suggests that each 1% increase in air content decreases concrete strength by 5%.

### High-Strength Concrete

In recent years, increased attention has been given to high-strength concrete, typically in the range of 60–70 MPa (Carino and Clifton 1990). Because this concrete is often made with w/c ratios less than 0.36 and usually with silica fume, there is reason to believe, as earlier discussed, that the resulting paste structure is so fine that any water entrapped in it cannot freeze at ordinary winter temperatures. Figure 5 shows that concrete rapidly becomes highly durable to freeze–thaw cycling at w/c ratios below 0.40, even when it is essentially non-air-entrained.



**Figure 5. Effect of distance between air bubbles vs. w/c ratio on the freeze–thaw durability of concrete. The open circles represent concrete mixtures that were undamaged by 300 rapid freeze–thaw cycles; the closed circles represent mixtures damaged by the same test. (After Okada et al. 1981.)**

Water-to-cement ratios below 0.36 in theory create a situation where no capillary pores can exist, while the silica fume converts calcium hydroxide, which adds no strength to concrete, into calcium silicate hydrate, the product that binds concrete together. This conversion alters the pore structure of concrete by producing smaller, fewer, and more discontinuous pores and creates stronger concrete, as might be expected (Table 1).

Table 1. Effect of silica fume on total pore volume.				
W/C	% SF by mass of cement	Pore volume* (mL/g)	Compressive strength† (MPa)	Frost resistance* (Durability Factor)
0.25	0	0.0232	65.9	98
	5	0.0228	NA**	95
	10	0.0236	81.7	95
	20	0.0255	87.1	95
	30	0.0271	NA	93
0.35	0	0.0353	51.5	82
	5	0.0335	NA	64
	10	0.0238	61.4	59
	20	0.0333	68.5	55
	30	0.031	NA	46
0.45	0	0.0593	NA	47
	5	0.0354	NA	45
	10	0.0442	NA	43
	20	0.0393	NA	20
	30	0.0403	NA	14

\* Yamato et al. (1986)  
 † Malhotra et al. (1987)  
 \*\* NA = not available

Concerning durability, Table 1 shows that at w/c ratios of 0.45, non-air-entrained concrete performed poorly and increasingly so with increasing silica fume content. At 0.35 w/c the concrete tested satisfactorily at 0 and 5% silica fume. At 0.25 w/c all non-air-entrained concretes performed excellently despite a bubble spacing that was four times that recommended by ASTM C 457. These data strongly suggest that concrete can adequately resist frost action without air entrainment. Philleo (1986), after reviewing the prospect of high-durability, non-air-entrained concrete, provided an opposing view by concluding that it is virtually impossible to make such a concrete consistently. The literature is divided.

Some investigators regard non-air-entrained, high-strength concrete to be inherently frost resistant (Traetteberg 1980, Sorenson 1983, Cheng-yi and Feldman 1985, Yamato et al. 1986, Kashi and Weyers 1989, Kukko and Matala 1990), but there are others who disagree (Malhotra et al. 1987, Yogendran et al. 1987, Fiorato 1989). About the only consensus among researchers is that the air entrainment parameters may be different for low-w/c concrete than they are for higher-w/c concrete. To solve this problem, researchers must either conduct more experiments to assess what these parameters might be or develop a new approach to improving the durability of concrete.

## 5 EFFECT OF DISSOLVED SOLIDS

The other factor common to frost damage, besides porosity, is the water. The two things that could be done to it to enhance the freeze–thaw durability of concrete are to reduce its volume, which was treated in the previous section of this report, or to lower its freezing point so that it doesn't freeze. Most standards caution against using admixtures to prevent freezing out of concern that the doses would have to be so high that they would harm the concrete in some way. However, very high doses of admixtures have been used in the former Soviet Union and elsewhere for winter protection with no apparent harm to the concrete (Korhonen 1990, Ramachandran 1995). The purpose of this section is to investigate what is known about the effects of dissolved solids in water in and near concrete.

### Chemical Admixtures

The deliberate use of chemical admixtures in concrete began with the introduction of air-entraining agents about 1938. Historically, admixtures go further back than that, as the Romans purportedly used animal fat and blood to improve workability. Nowadays, it is almost routine to incorporate chemical admixtures into fresh concrete to improve workability, alter setting times, inhibit metal corrosion, reduce cracking, and control water demand.

The amount and type of chemicals incorporated into concrete depend on the desired effect on the concrete. Table 2 was developed from manufacturers' literature along with a few assumptions to illustrate the approximate levels of additives used in concrete today. As can be seen, it is possible to incorporate nearly 10% dissolved solids into the mixing water by using only one admixture. Further, this concentration may increase with time because of loss of water to cement hydration. Multiple admixtures are often used in concrete, so the concentration of solutes in the water can be even higher than the individual values shown in Table 2. For example, Strand (1991) reported using six admixtures, five of which were of the chemical variety, for a concrete parking garage in Minneapolis. In an article describing how admixtures have changed concrete, Tarricone (1992) showed that concrete cannot get along without chemical admixtures today, and lots of them.

To be approved for use in concrete, chemical admixtures usually must pass a battery of tests to prove that they are harmless to the concrete. For example, and of special interest to this report, admixtures that satisfy ASTM C 494 requirements do not degrade the freeze–thaw resistance of concrete when used as specified by the admixture manufacturer. Thus, at the doses used today, admixtures do not appear to adversely affect the freeze–thaw durability of concrete.

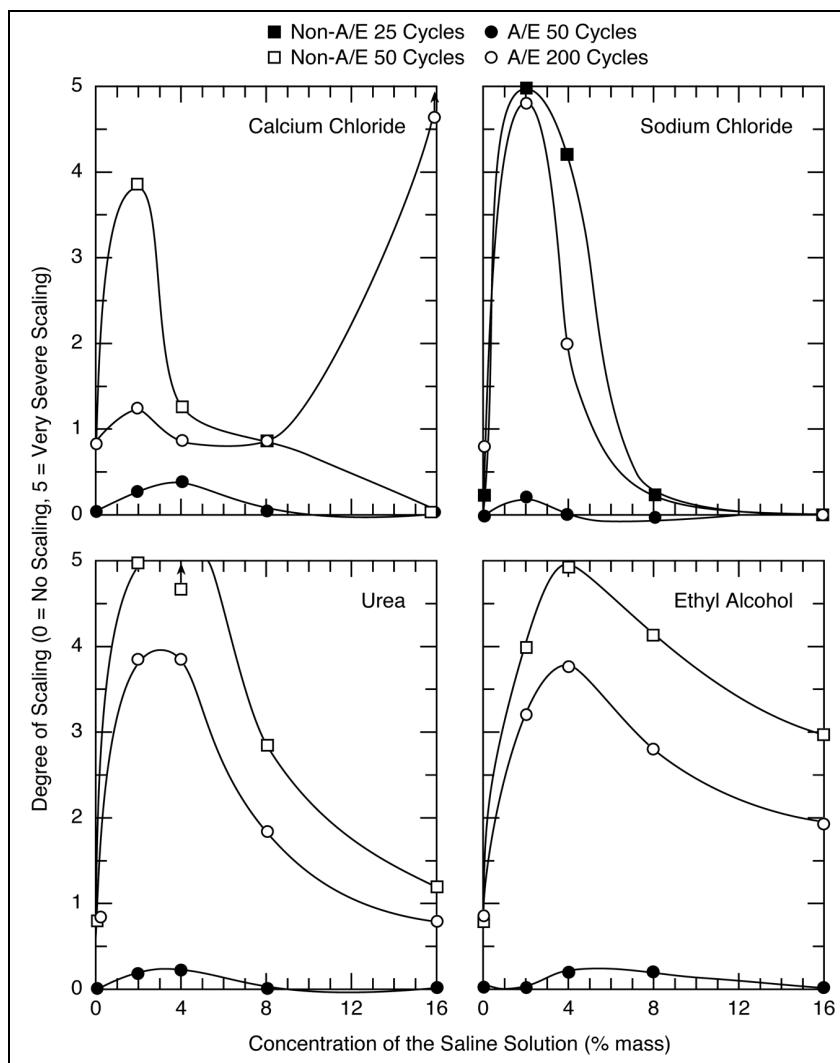
**Table 2. Typical admixtures routinely used in concrete today. The maximum doses are those recommended by the manufacturer.**

Admixture function	Dosage (mL/kg)	Concentration of active ingredient in mixing water (% mass basis)*	Concentration of active ingredient in pore water (% mass basis)†
Normal water reducer	2	0.2	0.26
Accelerator	125	8.5	10.4
Water reducer and accelerator	60	6.2	7.6
Superplasticizer	16	1.7	2.1
Corrosion inhibitor	125	8.5	10.4
Assumptions made to calculate concentrations:			
* The ratios of concrete ingredients were 1:3:2.4:0.5 (cement:coarse aggregate: sand:water) by mass, the admixtures are 40% active ingredient and the rest water, and the specific gravity of all admixtures is 1.30.			
† 75% of the cement is hydrated, water was neither lost nor gained from the concrete, and the active ingredient remains in solution.			

### Effect of De-icing Agents

It was during the 1920s and 1930s that the need for high-speed highways under all weather conditions created the need for de-icing salts (Whiting and Stark 1983). By mid-1930, however, many concrete pavements in the northern states had seriously scaled, presumably by the de-icing salts. The scaling, which usually developed within two years after salt was first used, was eventually related to the amount of salt applied to the road and the frequency of application. Numerous experiments conducted since then described the role that salt plays in the destruction of concrete pavement.

An early influential study in North America about salt action in concrete was done by Verbeck and Klieger (1957). To the upper surface of concrete slabs that had been saturated with plain water, they applied solutions of various concentrations before, during, and after freezing and observed their effects as a function of freeze–thaw cycle. One finding was that freezing and thawing a specimen with the salt solution on the surface was more damaging to the concrete than applying a salt solution to an already frozen specimen. The least severe response came from specimens that were frozen in a damp condition, after having removed the salt solution from the surface. Aside from proving that salt exacerbates surface scaling, the more interesting finding was that a solute concentration of 3–4%



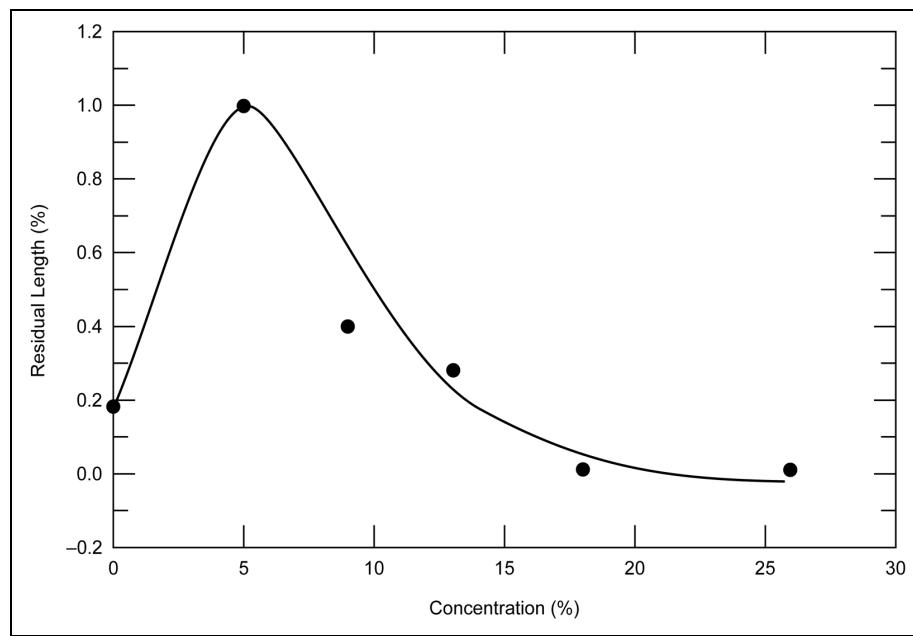
**Figure 6. Surface scaling vs. solution concentration for four chemicals. A/E stands for air-entrained. (After Verbeck and Klieger 1957.)**

produced more surface scaling than did higher or lower concentrations, including pure water. Verbeck and Klieger studied four chemicals and found that all were similar in action, demonstrating that surface scaling was a physical and not a chemical process (Fig. 6).

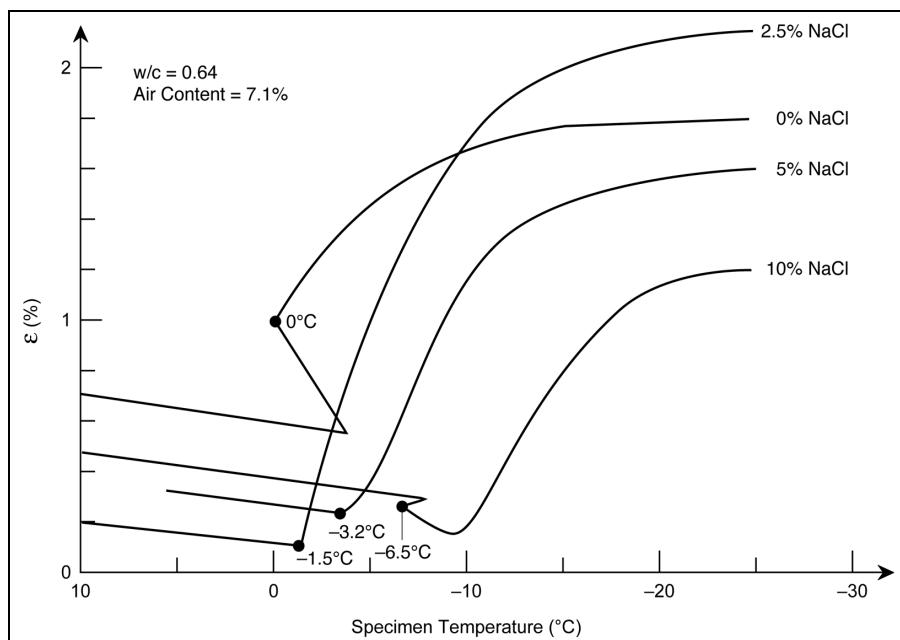
Other studies since then have found similar “pessimum” concentrations, which produce the most scaling. Litvan (1976), by measuring the length change of paste specimens as they cooled in a saturated condition inside a sealed testing cell, found that, when the paste was impregnated with NaCl solutions at various

concentrations, the length change curves were similar to those of specimens containing no salt, but they differed in magnitude. A plot of permanent length change, a good indicator of frost damage, from the length change curves in Litvan's paper shows that 5% salt solutions produce a maximum dilation that is five times larger than that of plain water (Fig. 7). Once the pessimum concentration was reached, higher concentrations produced progressively less scaling; at approximately 13% the damage was equal to that for plain water, and at higher concentrations scaling became even less pronounced. Fagerlund (1997) reported that mortar saturated with 5 and 10% NaCl solutions expanded less than did plain mortar. The largest expansion in his experiments occurred when the water in the pores of the mortar contained a 2.5% salt solution (Fig. 8).

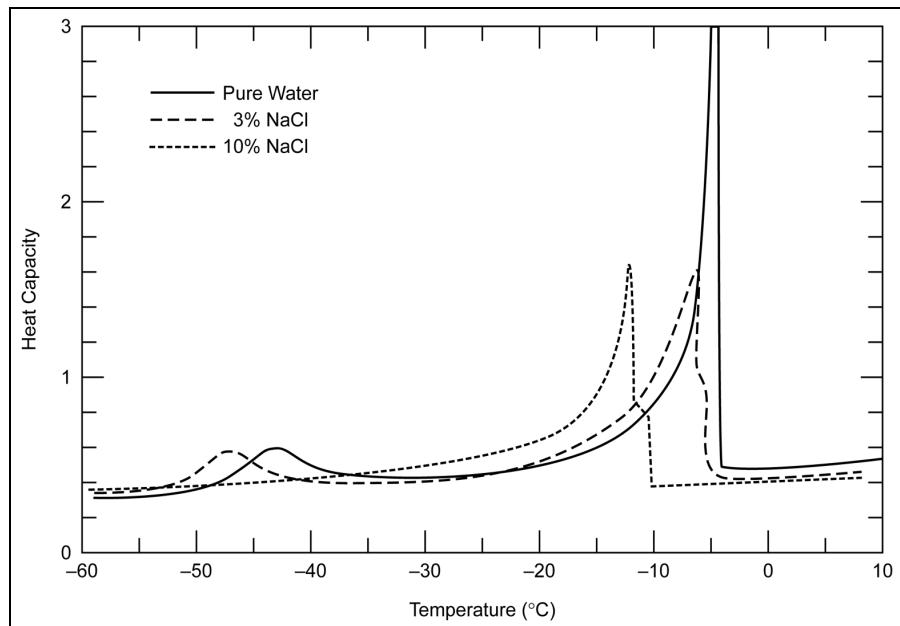
Sellevold and Farstad (1991) found that when salt solutions are applied to the outer surface of concrete, scaling is more pronounced for specimens that are water-saturated compared to those saturated with a salt solution prior to freeze–thaw testing. They also demonstrated through calorimetry studies that the freezing point of bulk water is depressed by the presence of dissolved ions in pure water. Figure 9 shows that the effect of dissolved salt on freezing point is superimposed on the freezing point depression caused by surface tension effects in the pores of hardened cement paste.



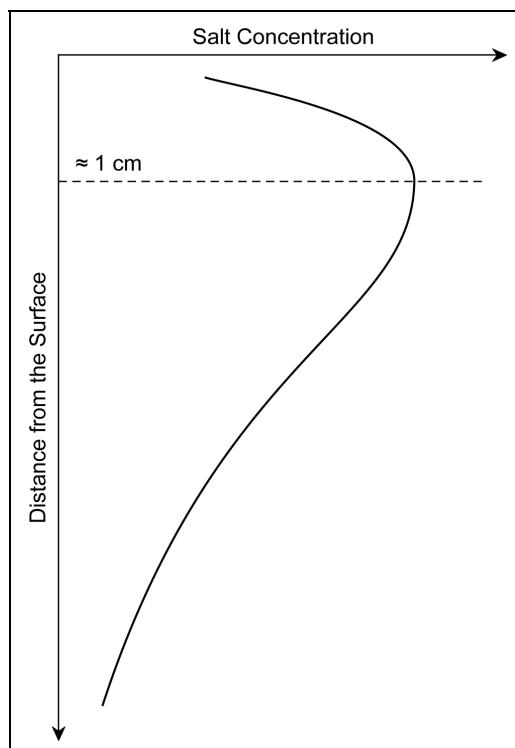
**Figure 7. Permanent change in length of cement pastes saturated with 0, 5, 9, 13, 18, and 26% NaCl solutions (by mass) cooled from 5 to  $-70^{\circ}\text{C}$  and back. (After Litvan 1976.)**



**Figure 8. Length change curves of mortar saturated with various concentrations of salt solutions. The temperatures for each curve indicate the initial freezing point of the solution in the mortars. (After Fagerlund 1997.)**



**Figure 9. Heat released from hardened cement paste (w/c 0.60) saturated with 0, 3, and 10% NaCl solutions. (After Sellevold and Farstad 1991.)**



**Figure 10. Salt gradient in a bridge deck.**  
(After Callahan et al. 1970.)

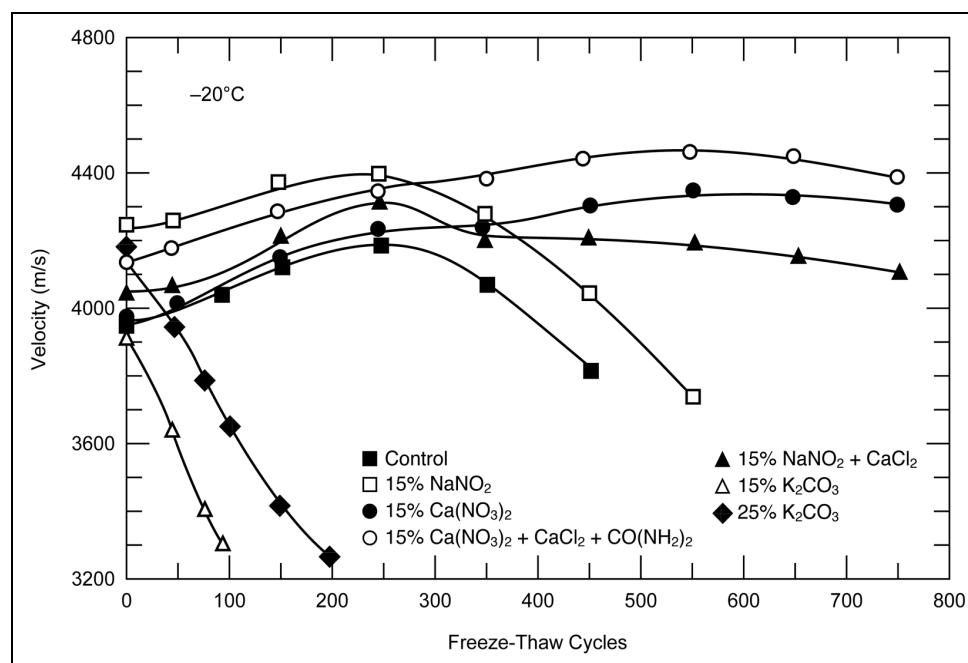
It is evident from these studies that salt solutions can either accelerate or retard frost damage, depending on the concentration of the solution that the concrete is subjected to. The observation for pavements has been that surface scaling worsens with the number of de-icer applications. Measurements recorded for bridge decks exposed to de-icing salts (Callahan et al. 1970) show that maximum chloride contents in the concrete ranged from 0.13 to 0.36% by weight of the mortar fraction in the concrete deck. Assuming that the chloride contents are based on oven-dry mortar that weighs  $1.26 \text{ g/cm}^3$  (oven-dry concrete weighs about  $2.3 \text{ g/cm}^3$ , of which 55% consists of mortar), that up to 18% by volume of the mortar contains water (Janoo et al. 1999), and that NaCl consists of 61%  $\text{Cl}^-$  by weight, then the field-measured chloride contents translate to 1.5–4.1% NaCl concentration in the pore water of the concrete bridge decks. The decks with the highest salt concentrations had the highest incidence of surface scaling. The 4.1% just calculated compares favorably to the pessimism concentrations of 2.5–5% reported above. This suggests that we are slowly poisoning our concrete by applying de-icing solutions to the roadways.

The salt is not concentrated near the surface but rather about 1 cm below the surface, as shown in Figure 10. It appears that some of this damage may be caused by a concentration gradient across the concrete. Scaling worsens when a pessimum gradient of around 3% is reached. The 3% gradient seems to amplify the normal process of water turning into ice through additional osmotic pressures near the surface of the concrete when freezing occurs, which creates an additional stress within the concrete. However, the pressures, and thus the damage, should become greater at higher concentrations but they don't. It may be that the freezing points of the higher-concentration solutions are sufficiently depressed so that as ice freezes out of solution, the freezing point of the remaining solution becomes low enough, soon enough so that very little ice forms at the lowest temperatures of the experiments (around  $-28^{\circ}\text{C}$ ). Thus, the primary stress on the concrete is that caused by osmosis plus the relatively small amount of ice that forms. From this it seems that salt in high enough concentrations in the pore water of concrete has a protective action.

### **Effects of High Admixture Concentrations**

Earlier it was said that the former Soviet Union and elsewhere use admixtures in dosages higher than those customarily used in North America for winter concreting purposes. Kukko and Koskinen (1988) described admixture added to fresh concrete in the range of 20% and above by weight of mixing water. These obviously are above the concentrations that exacerbate surface scaling, but not surprisingly scaling was not noted as a problem. In fact, freeze-thaw durability was usually reported as being superior to normal concrete. Figure 11 shows that only one of the six admixtures tested produced concrete that was less durable than control concrete.

It may be that all or most of the admixtures stay in the pore water solution; they probably do not combine with the hydration products. If this is so, the admixtures may depress the freezing point of the concrete so that it experiences fewer, or no, freeze-thaw cycles compared to normal concrete exposed to outdoor conditions. It could also be that the admixtures somehow prevent the mixing water from fully expanding, even though it freezes, so that less internal pressure is generated inside the concrete.



**Figure 11. Durability of non-air-entrained concretes made with various admixture concentrations given as percent by cement weight. (After Grapp et al. 1975.)**

## 6 CONCLUSIONS

It is commonly thought in North America that only air entrainment can truly guarantee good resistance to freezing and thawing. However, judging from test results of numerous researchers, it is clear that air entrainment only slows the freeze-thaw process; it does not prevent it. The advent of high-performance concrete with its low w/c ratio offers hope because any water entrapped in its fine microstructure should not freeze. Until more experiments are done to prove that high-strength concrete can be consistently produced in the field, specifications for concrete will continue to call for air entrainment.

The potential beneficial effects of pore water chemistry on freeze-thaw durability have been dismissed largely because of widespread pavement scaling that has been attributed to de-icing salts. There is no doubt that dissolved salts lead to surface scaling of concrete pavements in northern climates and that scaling is worst at a solute concentration of around 3%. However beyond a concentration of 3%, scaling becomes less severe, and concrete containing relatively high concentrations of dissolved salts fares better than does concrete with plain water in its pores. This suggests that perhaps concrete should initially be made with mixing water that contains more than 3% solutes. It should not matter what type of chemical was used, unless it was known to adversely affect concrete, as frost action in the presence of solutes is a physical and not a chemical process. In this manner the use of de-icing agents should not slowly build up to the point where they cause severe damage, but rather they could slowly make the pavement more resistant to frost action. Data from the former Soviet Union suggest that concentrations as high as 20% or more result in concrete that is significantly more durable than ordinary concrete.

## 7 WHAT'S NEEDED

Research is needed to investigate the effect of high doses of chemical admixtures on the freeze–thaw durability of concrete.

As previously discussed, freeze–thaw deterioration results from the combined effects of hydraulic and osmotic pressures. As soon as ice forms, it creates hydraulic pressure, which forces water to flow away from the freezing site, but it also concentrates dissolved particles in the solution near the ice, which causes water to flow toward the freezing site. Thus, the total pressure caused by water turning into ice is the sum of both phenomena.

As the concentration of dissolved particles is increased within the mix water, the amount of water that can freeze in the resulting hardened paste decreases. The less ice that forms, the less hydraulic pressure that results. However, the osmotic pressure, on the other hand, probably increases with each increase in solute concentration so that the combination of the two pressures should continue to increase until the amount of ice produced is so small that any increase in osmotic pressure cannot make up for the loss in hydraulic pressure. Thus, above some solution concentration, hardened paste should become increasingly more resistant to freezing and thawing. Ultimately, at some high concentration no ice should be able to form inside the paste, and frost damage should not be a problem. There may be an upper limit to the amount of solutes that can be incorporated into concrete before deterioration once again becomes a problem.

It is envisioned that by incorporating solute concentrations above some pes-simum amount into the mixing water of fresh concrete, the service life of the concrete can be extended.

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<p>The usual approach to increasing concrete's resistance to freeze-thaw damage is to modify its microstructure. Because concrete readily absorbs water, when it is in a wet environment and then cooled to below 0°C, any water that freezes inside the concrete will expand and, depending on the nature of the internal pore structure, could lead to internal micro-cracks. A single freezing event does not cause much harm, but repeated freezing and thawing cause the tiny cracks to grow and ultimately result in conspicuous cracks on the surface of the concrete, known as frost damage. This weakens the concrete and reduces its service life. There are several mechanisms responsible for this damage, so preventing it is complex. However, there are several practical methods used today to counteract problems caused by freezing water, including 1) incorporating entrained air into the concrete to relieve pressures caused by freezing water, 2) using low water-to-cement ratios to minimize the type of voids in which water typically freezes, and 3) using silica fume to refine the pore system so that water may not be able to freeze at normal ambient temperatures. This report reviews the frost damage mechanisms, considers the usefulness of current prevention techniques, and advances a new approach for making concrete resist the deleterious effects of freezing and thawing.</p>					
15. SUBJECT TERMS					
Antifreeze admixtures Cold-weather concreting		Freeze-thaw durability Low-temperature admixtures	Winter construction		
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	U	38	19b. TELEPHONE NUMBER (include area code)
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DEPARTMENT OF THE ARMY  
ENGINEER RESEARCH AND DEVELOPMENT CENTER, CORPS OF ENGINEERS  
COLD REGIONS RESEARCH AND ENGINEERING LABORATORY, 72 LYME ROAD  
HANOVER, NEW HAMPSHIRE 03755-1290

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